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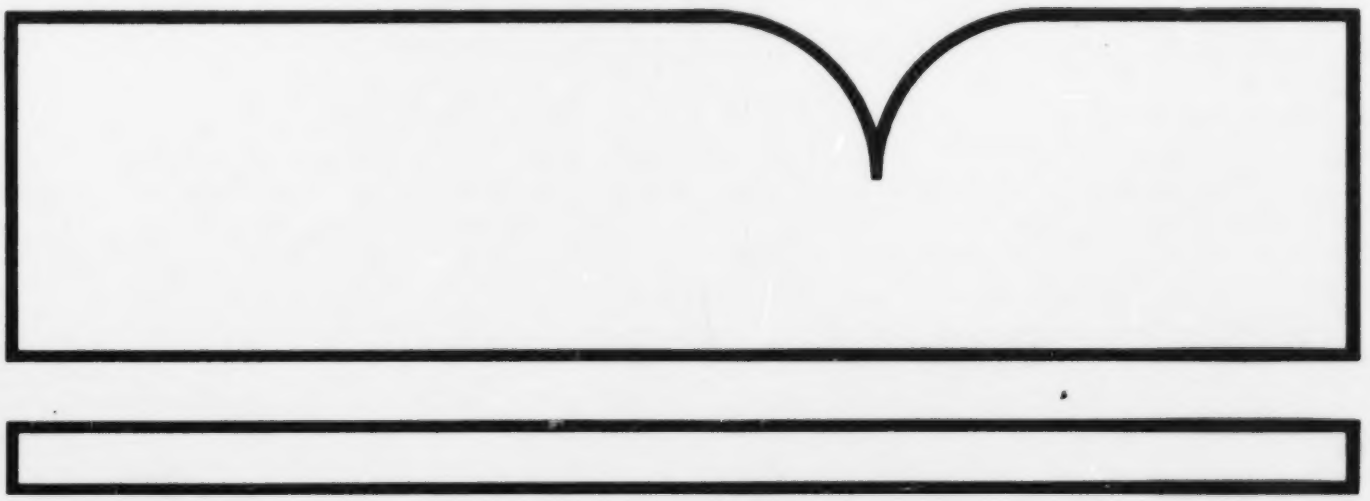

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16. ABSTRACT

A novel approach to quantitatively monitoring suspended hydrocarbons in water was conceived at Southwest Research Institute in 1975, and feasibility was subsequently demonstrated under sponsorship of the U. S. Environmental Protection Agency through Grant R804368-01. This new oil-in-water monitor technique brings together for the first time two previously unrelated technologies: (1) reversed-phase liquid chromatography and (2) fiber optics. A special organophilic optical fiber, created by a chemical treatment process routinely used in reversed-phase liquid chromatography, collects and concentrates suspended hydrocarbon materials on its surface. Collected material alters optical transmission through the fiber in such a way that the logarithm of the time rate of change of the logarithm of optical transmission through fiber is linearly proportional to the logarithm of contaminant concentration, provided that concentration exceeds a certain detection threshold.

Various methods of chemically treating an optical fiber and various treatment reagents were evaluated. Numerous treated optical fibers were tested individually, each with a variety of separate aromatic hydrocarbon contaminants, in a newly designed capillary-tube sensor cell. Additionally, a laboratory demonstration instrument employing the organophilic optical fiber hydrocarbon-in-water monitor technique was fabricated and tested. For such aromatic hydrocarbons as n-hexylbenzene, cyclohexylbenzene, heptadecylbenzene, 3, 3'-dimethylbiphenyl, and 1-phenylnaphthalene and for crude oil, detection thresholds of less than 3 mg/L were observed, and system response was linear over a contaminant concentration range of greater than 2.5 decades (*i.e.*, greater than 300:1). Data indicate that the high end of the range can be extended if desired.

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Phase II

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August 1980

DEVELOPMENT OF OIL-IN-WATER MONITOR PHASE II

by

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Grant Number R805817-01

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Test and investigate automated monitoring devices which will be both anticipatory as well as responsive to the needs of the Agency whose mandate is to restore, enhance, and protect the quality of the environment.

This report describes the preliminary investigation of an on-line continuous flow oil-in-water monitor developed by the Southwest Research Institute.

Dwight G. Ballinger
Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

A novel approach to quantitatively monitoring suspended hydrocarbons in water was conceived at Southwest Research Institute in 1975, and feasibility was subsequently demonstrated under sponsorship of the U. S. Environmental Protection Agency through Grant R804368-01. This new oil-in-water monitor technique brings together for the first time two previously unrelated technologies: (1) reversed-phase liquid chromatography and (2) fiber optics. A special organophilic optical fiber, created by a chemical treatment process routinely used in reversed-phase liquid chromatography, collects and concentrates suspended hydrocarbon materials on its surface. Collected material alters optical transmission through the fiber in such a way that the logarithm of the time rate of change of the logarithm of optical transmission through fiber is linearly proportional to the logarithm of contaminant concentration, provided that concentration exceeds a certain detection threshold.

Various methods of chemically treating an optical fiber and various treatment reagents were evaluated. Numerous treated optical fibers were tested individually, each with a variety of separate aromatic hydrocarbon contaminants, in a newly designed capillary-tube sensor cell. Additionally, a laboratory demonstration instrument employing the organophilic optical fiber hydrocarbon-in-water monitor technique was fabricated and tested. For such aromatic hydrocarbons as n-hexylbenzene, cyclohexylbenzene, heptadecylbenzene, 3, 3'-dimethylbiphenyl, and 1-phenylnaphthalene and for crude oil, detection thresholds of less than 3 mg/L were observed, and system response was linear over a contaminant concentration range of greater than 2.5 decades (*i.e.*, greater than 300:1). Data indicate that the high end of the range can be extended if desired.

The reported work was sponsored by the Environmental Monitoring and Support Laboratory, Office of Research and Development, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268, under Grant R805817-01. Portions of the reported work were conducted in the facilities of the U. S. Army Fuels and Lubricants Research Laboratory which is located at Southwest Research Institute and is operated under contract for the U. S. Army Mobility Equipment Research and Development Command, Ft. Belvoir, Virginia.

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SECTION I

INTRODUCTION

Waste water from such sources as refineries, shale-oil recovery plants, coal-conversion operations, chemical plants, ships, offshore drilling platforms, petroleum-handling facilities, and other industries may contain harmful quantities of hydrocarbon materials in suspension. Through programs coordinated and administered at the Federal level, a significant effort is underway to eliminate or substantially reduce the quantity of hydrocarbon material discharged in waste water. Treatment processes which remove suspended hydrocarbons from waste water have been placed in service by many organizations cooperating in water pollution control. While installation and operation of such treatment processes is a major step toward elimination of hydrocarbon pollution, to achieve maximum effectiveness it is necessary to monitor the effluent of a waste-water treatment process to insure that the system is functioning correctly. A simple, inexpensive, automated, on-line instrument is needed for this important monitoring function.

A new approach to quantitatively monitoring suspended hydrocarbons in water was conceived at Southwest Research Institute in 1975 (Ref.1). Feasibility demonstration and early development of this new concept was accomplished under sponsorship of the U. S. Environmental Protection Agency through Grant R804368-01 (Refs. 2 and 3). Briefly, this new oil-in-water monitor system employs a sensor cell through which a continuously flowing sample of the stream to be monitored is diverted. The sensor cell is similar to a reversed-phase liquid chromatographic column; however, in place of conventional column packing, the sensor cell contains a continuous unclad optical fiber, the surfaces of which have been made organophilic by chemical treatment. Suspended oil in the fluid flowing through the sensor cell is adsorbed on the optical fiber and (2) oil adsorbed on the fiber surfaces produces a change in the through-transmission attenuation factor of the optical fiber. Rate of decrease in optical fiber transmission is related to concentration of suspended hydrocarbons contaminating the stream being monitored.

The ultimate goal of developing the organophilic optical fiber oil-in-water monitor technique is to produce a reliable, simple to operate, easy to maintain and relatively inexpensive instrument for analysis of suspended hydrocarbons in water. Such an instrument could be employed in plants, on offshore platforms, aboard ships or in other facilities which generate hydrocarbon polluted waste water to monitor the effectiveness of treatment systems or to determine the quantity of pollutant being discharged. In the future, availability of an economical instrument for monitoring suspended hydrocarbons in water should result in increased awareness of the quantity of hydrocarbon material being discharged into streams or other bodies of water. This awareness should, in turn, increase industrial concern with water treatment and pollution prevention. Thus, the ultimate impact and benefit of developing an analytical instrument employing the organophilic optical fiber technique should be a decrease in hydrocarbon pollution in areas where this problem is already severe and prevention of such pollution in new areas.

This report covers (1) development of the organophilic optical fiber oil-in-water monitor concept, (2) improvement of the chemical treatment process and investigation of various treatment reagents, (3) extensive test of variously treated organophilic optical fibers with a wide range of hydrocarbon contaminants, (4) substantial improvement in sensor cell performance, and (5) fabrication of an engineering model instrument employing the organophilic optical fiber hydrocarbon detection principle. Substantial increase in sensitivity (by a

factor of 260) above that obtained in Phase I (Ref. 2) was realized during this program. Additionally, a detection threshold of less than 3 mg/L of crude oil (and some pure hydrocarbon compounds) in water was observed. Further details of the research and development work performed in accomplishing these results are presented in the remainder of this report.

SECTION II

OBJECTIVES

The objectives of the reported research work were (1) to further investigate experimentally the organophilic optical fiber concept as applied to measurement of suspended hydrocarbon material in water, and (2) to fabricate an engineering model instrument suitable for demonstration and test purposes having sensitivity at least as good as that achieved during early development in Phase I (*i.e.*, 50 to 100 mg/L detection threshold for tetralin).

SECTION III

SUMMARY

1. A new sensor cell employing an organophilic optical fiber contained in a coiled stainless steel capillary tube was designed, fabricated, and tested; sensitivity of this new sensor cell to tetralin exceeded that of the U-tube sensor cell used in Phase I by a factor of 260, and a detection threshold of less than 3 mg/L of crude oil in water was observed.

2. Modifications were made in the test apparatus to improve sensor cell performance and reduce the time required to conduct tests of various combinations of fiber material, treatment reagent and process, and hydrocarbon contaminant.

3. Improved chemical treatment apparatus was developed which facilitated faster processing with smaller quantities of treatment reagents and less potentially damaging handling of the optical fiber.

4. The chemical treatment process was improved by reducing the number of steps required and by converting to a flowing-reagent system.

5. Performance of the organophilic optical fiber sensor cell was characterized by conducting a large number of tests with a wide range of aromatic hydrocarbon compounds, crude oil and diesel fuel.

6. Contacts were made with manufacturers of fluoride glass to determine whether that material was potentially useful in the organophilic optical fiber oil-in-water monitor system.

7. A laboratory demonstration hydrocarbon-in-water monitor instrument was fabricated.

SECTION IV

CONCLUSIONS

1. Use of a coiled capillary-tube sensor cell to (1) increase active (i.e., curved) length of fiber, (2) eliminate optical cross-coupling and (3) improve contact between the fiber and test fluid increased system sensitivity by a factor of 260 for tetralin, but did not significantly change the detection threshold for this contaminant.

2. Response of the system to some contaminants, such as crude oil and n-hexylbenzene, was linear over a 2.5-decade range of concentration with a detection threshold of less than 3 mg/L.

3. A linear functional relationship between (1) the logarithm of the time rate of change of the logarithm of optical transmission through the organophilic optical fiber and (2) the logarithm of contaminant concentration was observed.

4. The organophilic optical fiber sensor cell is not uniformly sensitive to all hydrocarbon contaminants within its detection range, and no correlation was found between sensitivity and (1) refractive index of the contaminant, (2) ratio of refractive indexes of contaminant and fiber material, or (3) difference between refractive indexes of contaminant and fiber material.

5. Use of a fused-silica fiber facilitates detection of the widest range of hydrocarbon compounds; most aromatics can be detected by a fused-silica fiber, but all normal paraffins are excluded from detection.

6. Threshold of detection for a particular contaminant appears to be slightly greater than the solubility of that material in water.

7. An organophilic optical fiber can be cleaned and regenerated repeatedly without degradation.

8. Fluoride glasses are not presently practical in the organophilic optical fiber oil-in-water monitor because of solubility and chemical treatment problems.

9. Organic polymer fibers of types which have suitable surface properties for oil-in-water monitor applications are not available with sufficient optical clarity for practical use.

10. A low-power laser is the best illumination source for the organophilic optical fiber sensor cell because of the high efficiency with which light can be coupled into the fiber.

SECTION V

RECOMMENDATIONS

1. Optical fibers, treated with many different coating reagents used both singly and in combination, should be tested with a wide range of contaminants to establish definitive performance data which can provide a firm basis for selecting the optimum coating reagent for a particular application.

2. Use of non-visible radiation in the organophilic optical fiber should be investigated so that the infrared absorption, ultraviolet absorption, and ultraviolet-stimulated fluorescence effects characteristic of aromatic hydrocarbons may be evaluated with the objective of increasing sensitivity and specificity of the system.

3. The possibility of applying special coatings to optical fibers to facilitate adsorption of dissolved (in addition to suspended) contaminants from water should be investigated; sophisticated coating reagents which have surfactant, coagulant, or anticoagulant properties may be required.

4. The effects of increasing optical fiber diameter should be explored since such an increase would make coupling of light into the fiber easier and, perhaps, facilitate practical use of a non-laser illumination source.

SECTION VI

DISCUSSION

REVIEW OF CONCEPT

The organophilic optical fiber hydrocarbon-in-water monitor concept has been described fully in previous reports (Refs. 2 and 3). However, a brief review is included in this report for completeness.

Optical fibers are usually of coaxial construction as illustrated in Figure 1. The central part of the fiber, referred to as the "core", is surrounded by a tight-fitting sheath, referred to as the "cladding", which has lower index of refraction than the core. Sometimes a protective jacket of plastic or other material is applied over the cladding to increase mechanical strength of the fiber and to make the fiber easier to handle. A light ray entering the core of the fiber within a cone defined by the acceptance angle (illustrated in Figure 2) strikes the boundary between the core and the cladding at an angle greater than the critical angle so that total internal reflection occurs. Total internal reflection is highly efficient, so such a ray is transmitted through the core with low attenuation by successive reflections at the core-cladding interface. The acceptance angle is a function of the indexes of refraction of (1) the core material, (2) the cladding material, and (3) the medium in which the fiber is immersed (often air).

In the organophilic optical fiber oil-in-water monitor, an unclad optical fiber is used, that is, a fiber which has only a core and no cladding or protective jacket. The optical transmission properties of an unclad fiber are highly sensitive to the medium in which the fiber is immersed since that medium effectively functions as the fiber cladding. If the medium has lower index of refraction than the core material, then light entering the fiber within the acceptance angle cone will be retained within the fiber by total internal reflection and will be transmitted with relatively low attenuation to the opposite end of the fiber. If, on the other hand, the surrounding medium has greater index of refraction than the core material, then total internal reflection does not occur, and light entering one end of the fiber is rapidly dissipated into the medium. To provide for detection of hydrocarbon materials suspended in water, an unclad optical fiber is utilized which has greater index of refraction than water but lower index of refraction than the hydrocarbon materials to be detected. When such a fiber is in contact with water, it is effectively clad and, therefore, transmits light from one end to the other with low attenuation. However, when higher refractive index hydrocarbons deposit on the fiber surface, total internal reflection is locally degraded, and some of the light propagating in the fiber is lost through the fiber walls. As the quantity of hydrocarbon material accumulated on the fiber surface increases, efficiency of total internal reflection is further decreased, and more light escapes into the medium, thereby reducing intensity of the light arriving at the output end of the fiber. The degree to which total internal reflection is destroyed is related to the quantity of contaminant (i.e., thickness and extent of adsorbed layer) deposited on the fiber surface. It was experimentally determined during Phase I (Ref. 2) that the optical fiber must be curved for significant light loss to occur.

To make this phenomenon useful in an analytical instrument, it is merely necessary to provide a constant-intensity light source at the input end of the fiber and a photosensor at the output end to convert light emitted from the fiber into a proportionate electrical signal. A flowing sample of the stream to be monitored is then passed over the optical iiber. If this stream contains only water with no hydrocarbon contamination,

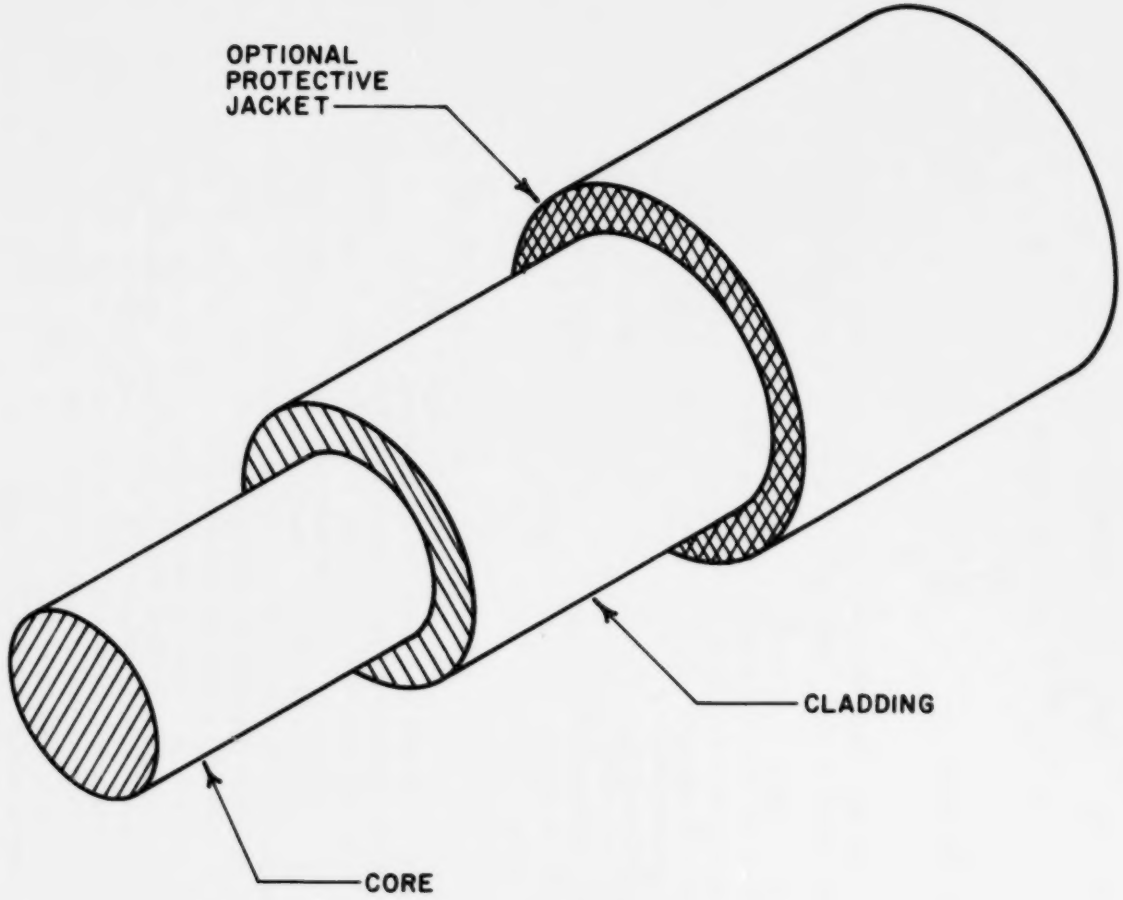

Figure 1. Typical Construction of Optical Fiber

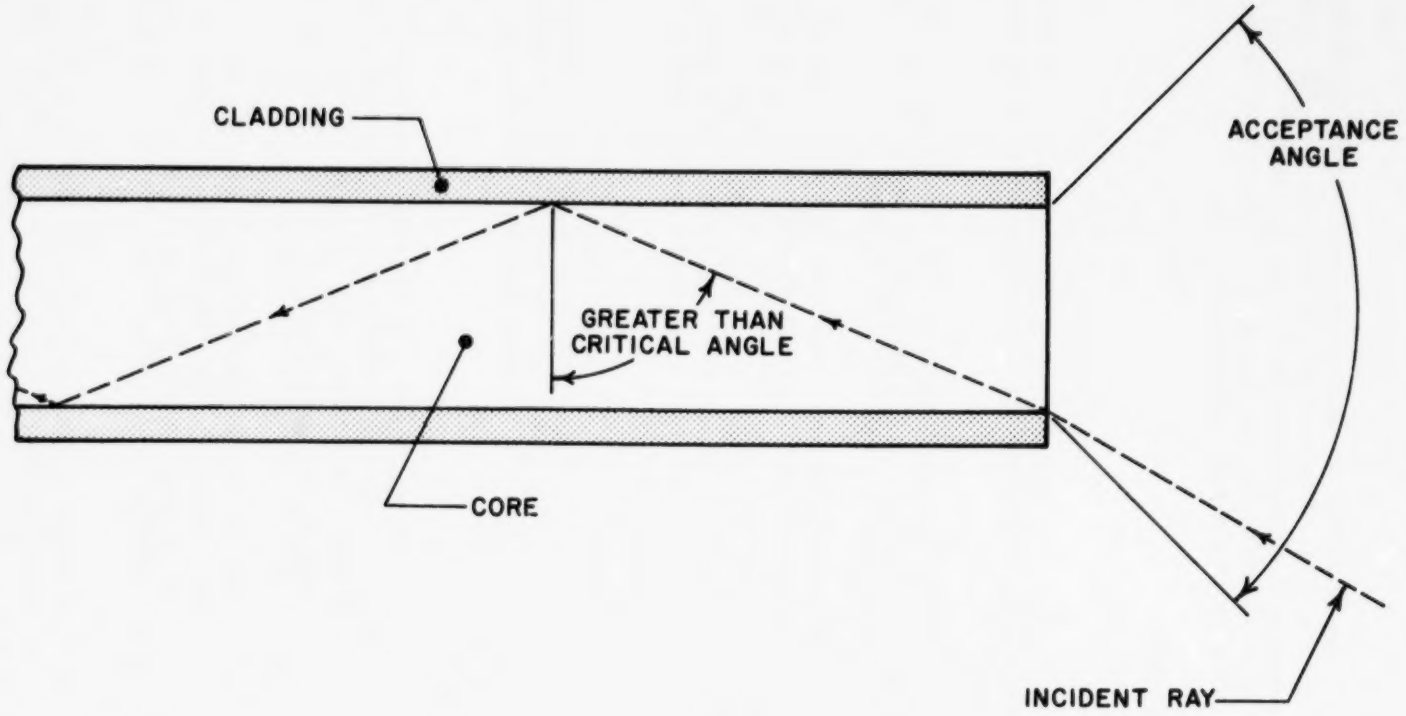

Figure 2. Cross-Section of Optical Fiber Showing Acceptance Angle and Typical Ray Path

then optical transmission through the fiber is unaffected. On the other hand, if there is hydrocarbon contamination present in the water, optical transmission through the fiber will decrease at a rate which is related to contaminant concentration.

To maximize the previously described effect, it is necessary to concentrate the available hydrocarbon contaminant on the optical fiber surface. This function is provided by making the optical fiber surfaces organophilic by use of a chemical treatment process similar to that employed in preparation of column-packing materials for reversed-phase liquid chromatography. Such treatment chemically bonds organic functional groups to the glass or fused-silica fiber material s illustrated conceptually in Figure 3.

PROCESS CHARACTERIZATION

Improved Apparatus

Chemical treatment of optical fibers was carried out by three methods designed to convert systematically from the method of Phase I to a method compatible with the capillary-tube sensor cell test apparatus used in this program (*i.e.*, Phase II).

The first method employed a process developed during Phase I (Ref. 2) in which batch treatment was conducted in a tubular, jacketed, glass reaction vessel. This apparatus was used for the first two fiber sets treated during Phase II to allow comparison between Phase I and Phase II systems.

The second method was compatible with the capillary-tube sensor cell configuration and facilitated coating the optical fiber in a capillary column. The capillary column containing the coated fiber was coiled and installed into the test apparatus after chemical treatment with minimal handling. Treatment apparatus included a stainless steel reservoir equipped with a dump valve and a flow-regulating needle valve. Stainless steel tubing conducted the various solvents and treatment reagents to a long, straight capillary tube containing the optical fiber to be processed. Two fiber sets were coated with this apparatus to develop the proper reagent/solvent solutions for compatibility with stainless steel.

The third method employed the same capillary column apparatus described above; however, the uncoated fiber was installed in a straight segment of capillary tubing which was coiled to fit the test apparatus before the fiber was coated to further minimize handling of the treated fiber. The treatment apparatus was also modified to coat three fibers simultaneously by installing a four-way cross in the flow system.

Procedures and Coating Experiments

By coating the fiber in the same capillary column used in the oil-in-water monitor device, possibility of damage to the optical fiber is minimized. Another benefit of treating fibers in a capillary tube is that reduced quantities of reagents are required. Further, more complete coating of the optical fiber occurs because (1) fresh reagent is constantly flowing through the system and (2) contact between the treatment reagent and the optical fiber is increased as a result of reduced reaction vessel volume.

The first set of fibers treated in Phase II comprised several 0.8-m-long crown-glass optical fibers which were coated by the glass-reaction-vessel method employed in Phase I of the program using a 100-mL-capacity glass chromatography column into which was placed a glass rod with fittings to hold the optical fibers. The various solutions were added to the column, allowed to stand for a predetermined time period and then drained.

After installation of the fibers, the column and fibers were cleaned by soaking with solvents and were dried overnight with heated helium. The next day, the column was allowed to cool, and the coating solution was added. After a 2-hr reaction time, the solution was drained. The coating solution was followed by several solvent sets to wash away excess coating reagent and reaction by-products. The fibers were then dried over-

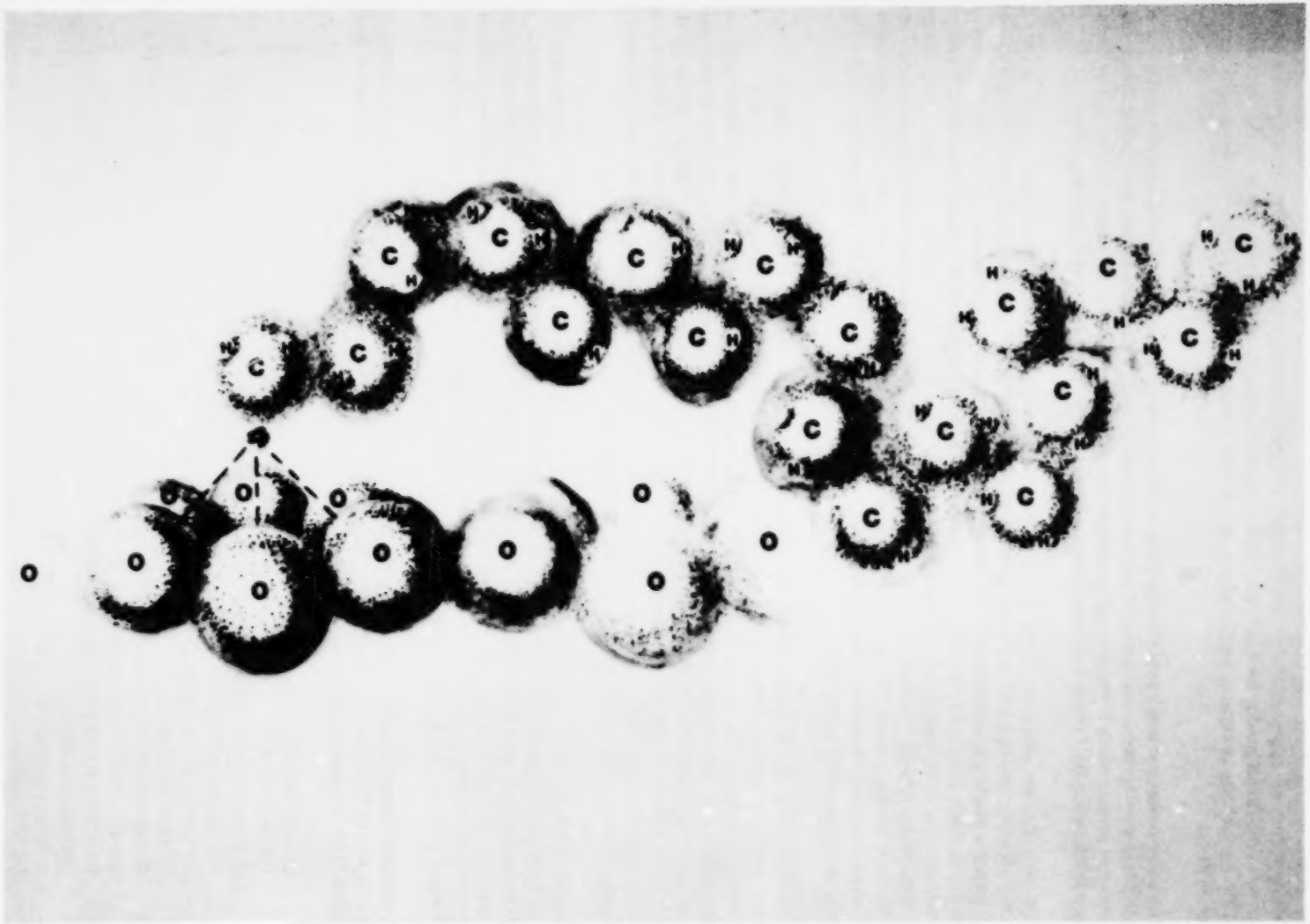

Figure 3. Possible Structure of Octadecylsilyl Group Bonded To Glass Surface

night by heated helium to remove the last traces of solvent. The coating reagent used for this fiber set was a v/v mixture of 80% octadecyltrichlorosilane and 20% octadecyltriethoxysilane. Fibers treated by this method were tested in the redesigned sensor-cell apparatus described later. By starting with a fiber similar to the ones used in Phase I of the program, performance of the new detection unit could be compared with results achieved in Phase I.

The second fiber set was coated in the glass chromatography column utilizing the solution sets planned for use in the metal capillary-tube system. The coating reagent used was octadecyltrichlorosilane. This experiment was run to determine if the change in solvent systems would make a difference in fiber performance and to set the baseline for further experimentation with octadecyltrichlorosilane as a coating reagent.

The third fiber set was coated with octadecyltrichlorosilane in the straight metal capillary column apparatus. Operationally, the optical fiber was installed in a suitable length of capillary tubing, and this tubing was coupled into the treatment apparatus. The reservoir was filled with a cleaning solution which was then forced through the capillary tube until the supply was exhausted. Rinsing solutions were passed through the system in a similar manner. The interior of the treatment apparatus was then dried overnight by passage of heated helium through the tubing. The next day, the silane treatment reagent and subsequent rinsing solutions were forced through the apparatus. The interior of the treatment apparatus and fiber were dried overnight by passage of heated helium. To assist in overcoming heat loss through the metallic walls of the apparatus, the reservoir was wrapped with heating tape.

The fourth fiber set also was coated with octadecyltrichlorosilane in the straight metal capillary column apparatus. In this treatment, however, the hydrogen chloride by-product was scavenged by tri-n-octyl amine in the coating solution. The standard scavenger, pyridine, was unsuitable because the pyridine-hydrogen chloride reaction product was insoluble in toluene and would have clogged the capillary. Several amines were screened, and tri-n-octyl amine was found to be very satisfactory. This amine does not have an active hydrogen, so it does not react with the organosilane compound, and it also has sufficiently long alkyl groups that the tri-n-octyl amine-hydrogen chloride salt is soluble in toluene despite its polarity. The organosilane coating solution contained enough amine to neutralize the hydrogen chloride formed.

Eight sets of optical fibers were chemically treated by various reagent solutions in the coiled capillary system. The first fiber set treated in the coiled capillary column yielded three fibers which had low response in the test apparatus believed to be caused by insufficient coating reagent. For the second set, concentration and amount of coating reagent were increased so that each fused-silica fiber in the apparatus received the same amount of coating reagent as one fiber had in the earlier straight-capillary column method. Coating reagent flow rate was also decreased to allow increased reaction time.

Additional fused-silica fibers were coated with various reagent/solution systems to test the effects of different chemical coatings and methods of application. The various coating solution systems are listed below. One fiber was coated with each.

1. Octadecyltriethoxysilane (coating reagent)
   Toluene (solvent)
2. Octadecyltriethoxysilane (75% v/v, coating reagent)
   Octadecyltrichlorosilane (25% v/v, coating reagent)
   Tri-n-octyl amine (hydrogen chloride scavenger)
   Toluene (solvent)
3. Octadecyltriethoxysilane (95% v/v, coating reagent)
   Octadecyltrichlorosilane (5% v/v, coating reagent acting mainly as catalyst)
   Tri-n-octyl amine (hydrogen chloride scavenger)
   Toluene (solvent)
4. Octadecyltriethoxysilane (95% v/v, coating reagent)
   Trimethylchlorosilane (5% v/v, coating reagent acting mainly as catalyst)
   Tri-n-octyl amine (hydrogen chloride scavenger)

Toluene (solvent)

5. Octadecyltriethoxysilane (coating reagent)
   Isopropanol (solvent)
   Water (catalyst)

The octadecylsilyl group was applied to most of the fibers treated during the program. This alkyl group can be applied with ethoxy or chloride as the leaving group. The chloro and ethoxy reagents were used both singly and in mixtures. Trimethylchlorosilane (TMCS) has been used successfully as a silylation catalyst in analytical chemistry. In this program, octadecyltrichlorosilane was used instead of TMCS as a catalyst to aid in fiber coating (Fibers C and D, Table I). Also, isopropanol was tried as a solvent for octadecyltriethoxysilane because this material is compatible with the alcohol where the chlorosilane is not. Additionally, water was tried as a catalyst for octadecyltriethoxysilane in alcohol.

TABLE I. IDENTIFICATION OF TEST FIBERS

Fiber	Coating Reagent Composition
A	Octadecyltrichlorosilane
B	Octadecyltriethoxysilane
C	Octadecyltriethoxysilane 75% Octadecyltrichlorosilane 25%
D	Octadecyltriethoxysilane 95% Octadecyltrichlorosilane 5%
E	Octadecyltriethoxysilane isopropanol and water as solvent)
F	Diphenyldichlorosilane
G	n-Decyltrichlorosilane

FIBER EVALUATION

Test Apparatus

It was experimentally determined (Ref. 2) that an organophilic optical fiber must be curved to be highly active in attenuating transmitted light as hydrocarbon material collected on its surface. To maximize the effect of this property, attempts were made in the previous program (Ref. 2) to fabricate a multi-turn optical fiber coil so that a much greater curved length could be obtained. Tests with this device indicated increased sensitivity, but the degree of increase was not as great as expected. Optical cross-coupling between turns of the coil and inefficient contact between the flowing fluid and the fiber surface were postulated as possible explanations for these observed results. In designing the sensor cell to be used in the test apparatus for this program, particular consideration was given to (1) increasing the active (*i.e.*, curved) length of optical fiber, (2) eliminating optical cross-coupling between turns of the fiber coil, and (3) achieving substantial increase in contact between the flowing fluid and the fiber surface.

The resulting experimental sensor cell, illustrated in Figure 4, comprised a coil of 1.59-mm (0.0625-in.) O.D. by 0.58-mm (0.022-in.) I.D. stainless steel capillary tubing containing a 0.13-mm (0.005-in.)-diameter optical fiber in its interior. Approximately 5% of the cross-sectional area of the capillary tube lumen was occupied by the optical fiber. The fluid sample to be tested was flowed through the capillary tubing so that it came in close contact with the fiber surface. By coiling the fiber-containing capillary tube, any desired active length could be achieved. Additionally, with the fiber contained inside an opaque tube, cross-coupling between turns of the coil was entirely eliminated.

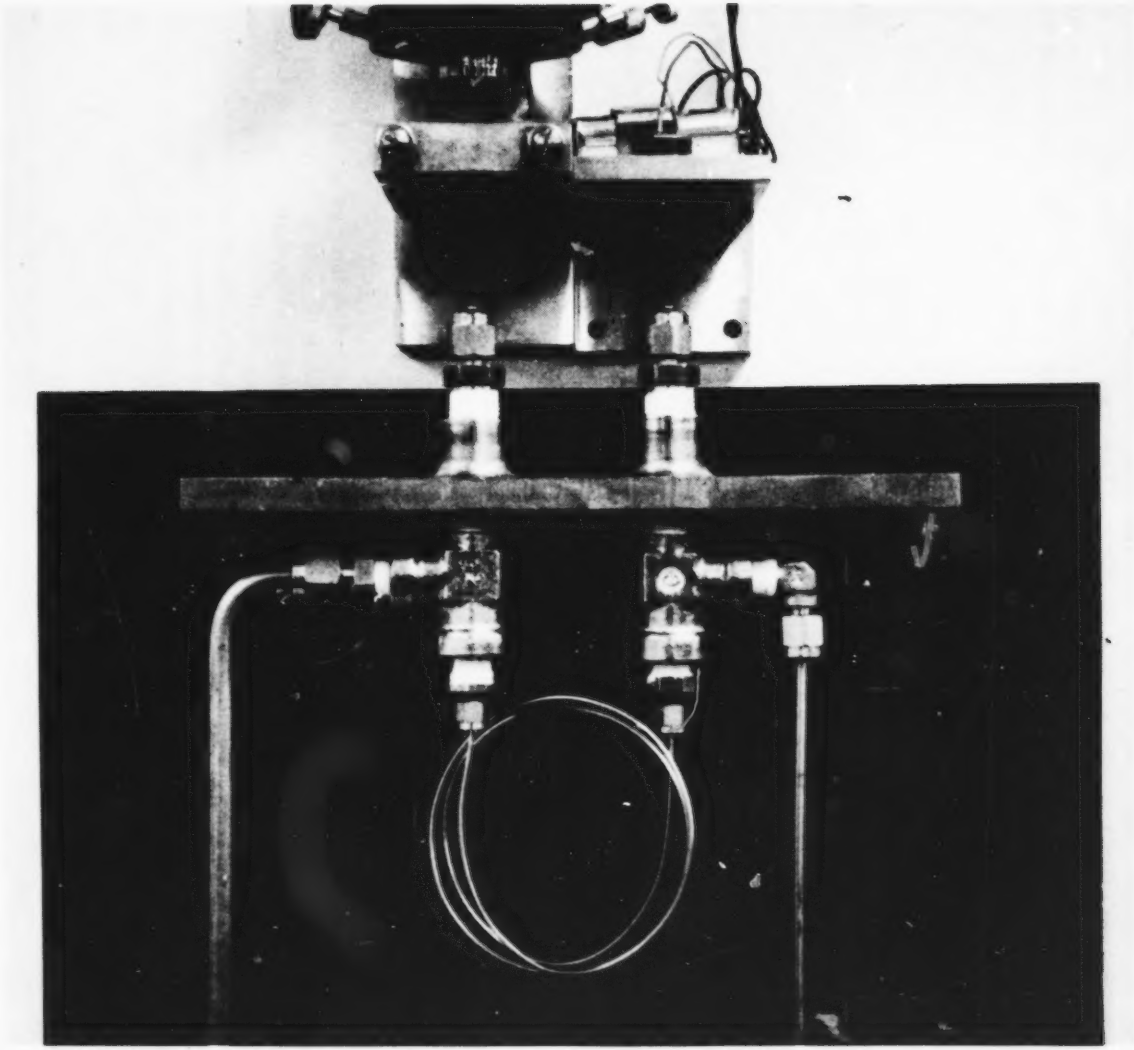

Figure 4. Close-Up View of Capillary-Tube Sensor Cell and Fluid Connections

To facilitate quantitative testing, the coiled capillary tube sensor cell containing the optical fiber was installed in the test apparatus shown schematically in Figure 5 and illustrated in Figure 6. The capillary tube was connected to the fluid handling apparatus by means of compression-type tube fittings, and the ends of the fiber were brought out through seals. The beam from a low-power helium-neon laser was reflected by a 90° prism through a microscope objective and brought to focus on the input end of the organophilic optical fiber under test. Optical energy emitted from the output end of the fiber was directed on the sensitive area of a silicon PIN (positive-intrinsic-negative) photodiode. A power supply was provided to bias the photodiode, and a commercial electrometer was used to measure diode photocurrent. Electrometer output was recorded on a commercial strip-chart recorder having logarithmic amplitude response.

A reservoir was provided to contain the test fluid. Compressed air, obtained from a 700-kPa (100-psi) supply through a filter-separator and pressure regulator, was admitted to the sealed reservoir above the liquid surface. Various valves provided for (1) pressurizing and venting the reservoir, (2) draining and flushing liquid from the reservoir, and (3) controlling fluid flow through the capillary-tube sensor cell. A graduated cylinder was used to collect system effluent for the purpose of determining average flow rate. Tubing, fittings, valves, etc. in the fluid-flow path were made of 300-series stainless steel.

Test Suspension Preparation and Materials

Test suspensions used to evaluate chemically treated fibers in the test apparatus were prepared using an ultrasonic disperser. A 1000-mg sample of the hydrocarbon contaminant to be used was added to 1L of deionized water in a glass vessel. Cavitation produced by a Sonicator horn broke the contaminant into very fine particles which remained suspended for several hours. Dilutions were made from the prepared stock to obtain a series of suspensions in half-decade steps of concentration (i.e., 1000, 300, 100, *etc.* mg/L). Because contaminant concentrations greater than 1000 mg/L were beyond the range of primary interest, concentrations greater than this value were not prepared or used. The lowest concentration was either 10 mg/L or 1 mg/L depending upon the particular contaminant.

A list of the contaminants used during this program is presented in Table II.

TABLE II. CONTAMINANTS EXAMINED BY TEST APPARATUS

Chemical Used as Contaminant	Refractive Index
Heptadecylbenzene	1.4798
Dodecylbenzene	1.4820
n-Hexylbenzene	1.4900
tert-Butylbenzene	1.4927
p-Xylene	1.4958
Ethylbenzene	1.4959
m-Xylene	1.4972
o-Xylene	1.5055
Chlorobenzene	1.5241
2,6-Dimethylstyrene	1.5315
Cyclohexylbenzene	1.5329
1,2,3,4-Tetrahydronaphthalene (Tetralin)	1.5414
Bromobenzene	1.5597
3,3'-Dimethylbiphenyl	1.5946
Phenanthrene	1.5973
1-Methylnaphthalene (alpha isomer)	1.6170
1-Phenylnaphthalene (alpha isomer)	1.6646
Diesel Fuel	—
Crude Oil	—

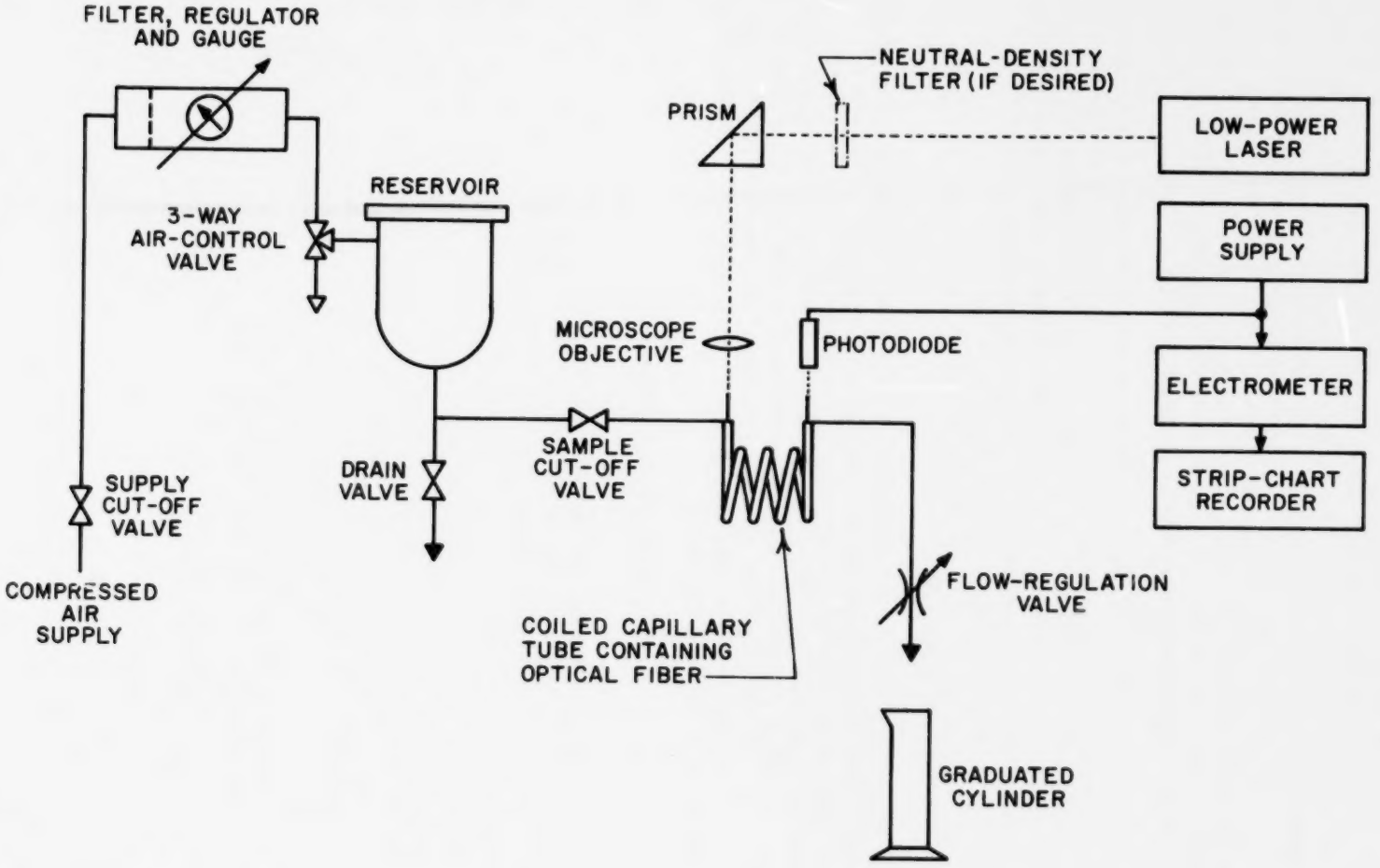

Figure 5. Schematic Diagram of Test Apparatus Including Coiled Capillary-Tube Sensor Cell

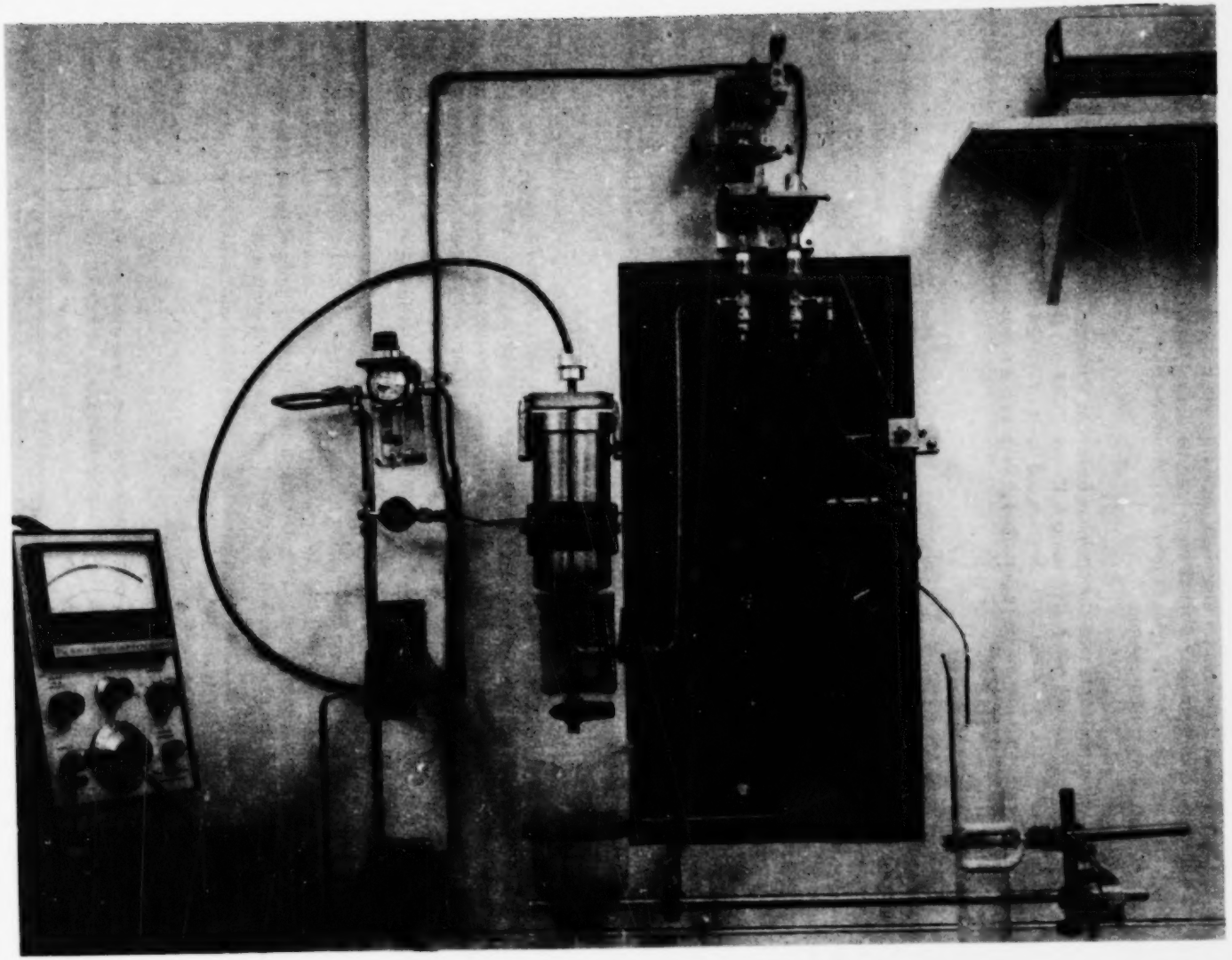

Figure 6. Photograph of Test Apparatus Employing Capillary-Tube Sensor Cell

Fiber Materials

During the time that the chemical treatment apparatus and process were being perfected, 0.13-mm (0.005-in.)-diameter crown-glass optical fibers were used because a large quantity of this material was left from Phase I. However, because the index of refraction of crown glass (1.5224) is relatively high, only a limited range of contaminants could be tested.

After preliminary experiments with the chemical treatment apparatus and procedure were completed, all subsequent experiments were conducted using 0.13-mm (0.005-in.)-diameter fused-silica optical fibers which had a refractive index of 1.4585. With this reduced value of refractive index, it was possible to use a wide range of hydrocarbon contaminants as described in the previous subsection.

Test Procedure

A chemically treated optical fiber contained in a coiled stainless steel capillary tube (*i.e.*, the sensor cell) was installed in the test apparatus previously illustrated in Figures 4 and 6. Typically, the stainless steel capillary tube was approximately 0.8 m (31 in.) long and was formed into a 3.5-turn coil of 70-mm (2.8-in.) inside diameter. The ends of the optical fiber projecting from the ends of the capillary tube were threaded straight through the tee fittings of the test apparatus and were passed through silicone rubber compression seals which retained the test fluid in the sensor cell.

After sensor cell installation, the apparatus was cleaned with successive washes of approximately 150 mL each of acetone and methanol. Cleaning solvents and test suspensions were forced through the sensor cell by 300-kPa (44-psi) compressed air introduced into the reservoir. Following the two solvents, 300 mL of deionized water was forced through the sensor cell to insure that all solvent was flushed from the system; flow was terminated before all of the water had been used so that the flow path remained filled with deionized water.

Test suspensions of a particular hydrocarbon contaminant in water were prepared in various concentrations as previously described. These test suspensions were introduced sequentially into the test apparatus reservoir beginning with the highest concentration. Each test suspension was forced through the sensor cell at a rate of approximately 0.5 mL/s until the fiber saturated or all of the test suspension was used. While the test suspension was flowing through the sensor cell, current through the photodiode was recorded on a strip-chart recorder. After use of each test suspension, the three-step clean-up procedure previously described was repeated. In most cases, this clean-up procedure restored optical transmission of the fiber to the value observed prior to introduction of any hydrocarbon contaminants.

Transmission loss occurring over a specified time interval was measured on the strip-chart record. This value of transmission loss in decibels (dB) was divided by the time interval in seconds (s) to obtain the slope of the line on the strip-chart record in units of decibels per second (dB/s). Slopes obtained with this procedure for a particular hydrocarbon contaminant were plotted on logarithmic graph paper as a function of contaminant concentration. Typical curves are presented later.

TEST RESULTS

Tests conducted during this program were intended to cover four main points: (1) comparison of the new capillary-tube sensor cell with the glass U-tube configuration used in Phase I (Ref. 2), (2) determination of the effects of various chemical treatment processes on performance of an organophilic optical fiber, (3) evaluation of various treatment reagents, and (4) measurement of sensor cell response to a variety of hydrocarbon contaminants at various concentrations. As previously noted, raw data from a series of tests involving a particular fiber and a single contaminant at various concentrations were translated into a graph relating the time rate of decrease of optical transmission through the fiber to contaminant concentration. This

graph, when plotted on logarithmic coordinates, typically was linear over a wide range of contaminant concentration. Examples of such curves are presented in later paragraphs to illustrate specific points.

Because the mathematical function which plots as a straight line on logarithmic coordinates is nonlinear if plotted in linear Cartesian coordinates, sensitivity (usually defined as the derivative of the function relating output to input) is not a constant and, hence, varies as a function of the independent variable (in the case of the organophilic optical fiber oil-in-water monitor system, the independent variable is contaminant concentration). Thus, for comparison purposes, sensitivity must be measured at a specific value of the independent variable. Throughout this report, sensitivity figures are specified for a contaminant concentration of 1000 mg/L. Details of the method used in calculating sensitivity figures given in this report are presented in Appendix A.

Comparison of Performance of Two Sensor Cell Designs

In designing a new sensor cell for this program, three significant changes were made with respect to the sensor cell previously employed in Phase I (Ref. 2) of the program: (1) contact between the test fluid and the organophilic optical fiber was greatly enhanced, (2) active (*i.e.*, curved) length of the optical fiber was increased, and (3) optical cross-coupling between turns of the coiled optical fiber was eliminated. Effects of these factors were not evaluated individually, but their combined influence on sensor cell sensitivity was determined. The curves in Figure 7 show data acquired with the glass U-tube sensor cell employed during Phase I (Ref. 2) and the new coiled capillary-tube sensor cell used in this program. In both cases, the contaminant was 1,2,3,4-tetrahydronaphthalene (tetralin). It is apparent that the response of the new sensor cell is substantially greater at any specified value of contaminant concentration and that the slope of the response curve for the new sensor cell is greater than that of the old sensor cell. Using the definition of sensitivity given in Appendix A, sensitivity of the new sensor cell at a contaminant concentration of 1000 mg/L is approximately 260 times the sensitivity of the U-tube cell at the same concentration. This increase in sensitivity should substantially reduce the effects of system noise.

Evaluation of Fiber Treatment Processes

As described in an earlier section, a transition from the chemical treatment apparatus and process employed in Phase I (Ref. 2) to the improved process and apparatus used during Phase II was achieved by a systematic progression of changes. The objectives of transition were to (1) simplify the process, (2) reduce the quantities of reagents consumed, (3) minimize handling of the fiber, and (4) reduce the time required to chemically treat a fiber. Optical fibers produced by each step in the transition progression were evaluated using the previously described test apparatus and procedure. The various chemical treatment processes and apparatus variations produced optical fibers which had equivalent sensitivities, indicating that the four objectives had been achieved.

Effects of Various Treatment Reagents

Several coating reagents, used singly and in combination (discussed in a previous section), were tried. Analysis of test data indicates that the method of applying the coating reagent and the reagent itself affect the capability of the optical fiber to adsorb hydrocarbons.

Fibers A, B, C, D, and E (refer to Table I for identification) were prepared to facilitate comparison of octadecyltrichlorosilane and octadecyltriethoxysilane coating reagents. The hydrocarbon chain left on the glass fiber is the same with these reagents, but the leaving group is different. With n-hexylbenzene as the test contaminant, better response was obtained with Fibers B, C, and E which were treated with octadecyltriethoxysilane; however, response of Fiber D, which was also treated with a triethoxy-based silylating reagent, was about the same as for Fiber A which was treated with a trichloro-based silylating reagent. With 1-methylnaphthalene as the test contaminant, Fibers B and C exhibited steeper response curve slopes than did Fiber A; however, the lower limit of detection of 1-methylnaphthalene was approximately 30 mg/L for fibers

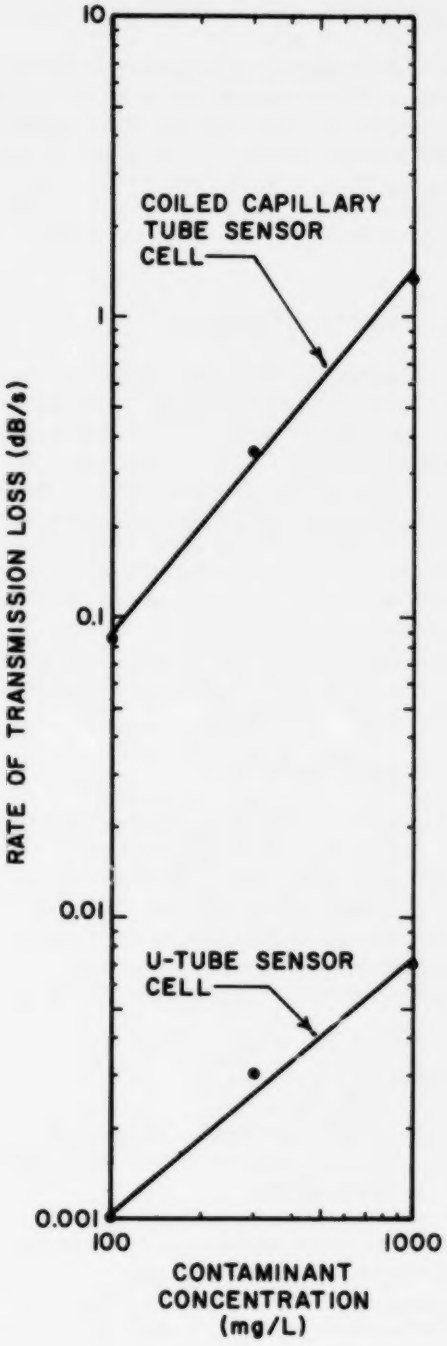

Figure 7. Comparison of Responses of Sensor Cells of Two Different Designs to Tetralin

treated with the trichloro-based reagent and between 30 mg/L and 100 mg/L for fibers treated with the triethoxy-based reagents. Sensitivity differences could not be correlated with the reagent leaving group. Further, sensitivities to various hydrocarbon contaminants were not the same for fibers treated with reagents containing different leaving groups.

Experiments were also performed with additional treatment reagents which left other hydrocarbon chain groups on the fiber. A diphenylsilane reagent was used on Fiber F, and an n-decylsilane reagent was used on Fiber G (see Table I for fiber identification). Test data indicate a potentially greater response curve slope for fibers treated with the diphenylsilane reagent. The lower limit of detection is approximately the same for fibers treated with diphenylsilane and octadecylsilane reagents. Fibers treated with the n-decylsilane reagent were not as sensitive as fibers treated with octadecyl or diphenylsilane reagents when n-hexylbenzene was the testing contaminant, but were more sensitive than fibers treated with the octadecylsilane reagent when the contaminant was crude oil.

For the present, the best coating reagent for use in the hydrocarbon-in-water monitor instrument appears to be octadecyltrichlorosilane. This reagent produces the best overall response to a wide variety of hydrocarbon contaminants. Because different contaminants do not produce uniform responses in fibers with various coatings, there does not appear to be an optimum coating reagent, among those tested, for all contaminants of interest.

Sensitivity to Various Contaminants

Numerous pure hydrocarbon compounds, previously listed in Table II, were employed as contaminants during evaluation and test of the new coiled capillary-tube sensor cell. The curves of Figure 8 illustrate sensor cell response to three such contaminants: (1) n-hexylbenzene, (2) tetralin (1,2,3,4-tetrahydronaphthalene), and (3) p-xylene. The curve for tetralin in Figure 8 is typical of the responses observed for many different contaminants; the curve is linear (on logarithmic coordinates) above a particular value of contaminant concentration (100 mg/L for tetralin) and falls off sharply below that value. The value of contaminant concentration at which system response (i.e., rate of transmission loss) is 0.001 dB/s is defined for purposes of this report as the "detection threshold". From the curves in Figure 8 it is evident that the detection threshold for n-hexylbenzene is about 2 mg/L; for tetralin, approximately 30 mg/L; and for p-xylene, slightly greater than 400 mg/L. Because the greatest contaminant concentration used in this program was 1000 mg/L, it is not known how far the linear range extends beyond this value. Data acquired during Phase I (Ref. 2) indicate that the response curve for tetralin is linear to a contaminant concentration of at least 7000 mg/L.

Although most tests of the organophilic optical fiber hydrocarbon-in-water monitor system were conducted using pure hydrocarbon compounds as previously noted, a few tests were conducted using diesel fuel and crude oil as the contaminant. The system was capable of detecting diesel fuel at a concentration of 17 mg/L. However, as illustrated in Figure 9, the system was highly sensitive to crude oil and had a detection threshold of less than 3 mg/L. Composition of the crude oil used in this experiment is described in Appendix B.

Sensitivity (defined in Appendix A) and detection threshold (i.e., contaminant concentration for which rate of transmission loss is 0.001 dB/s) varied from contaminant to contaminant. From the very limited data available, it appeared that detection threshold for a particular contaminant was related to solubility of that compound in water. A reasonable search of the literature produced very little specific solubility information because most hydrocarbon compounds which are less than 1% (10,000 mg/L) soluble in water are reported as "insoluble". Specific values of solubility in water at 25°C were found for only five of the hydrocarbon compounds used as contaminants during this program:

1-methylnaphthalene	30mg/L
m-xylene	170mg/L
o-xylene	200 mg/L

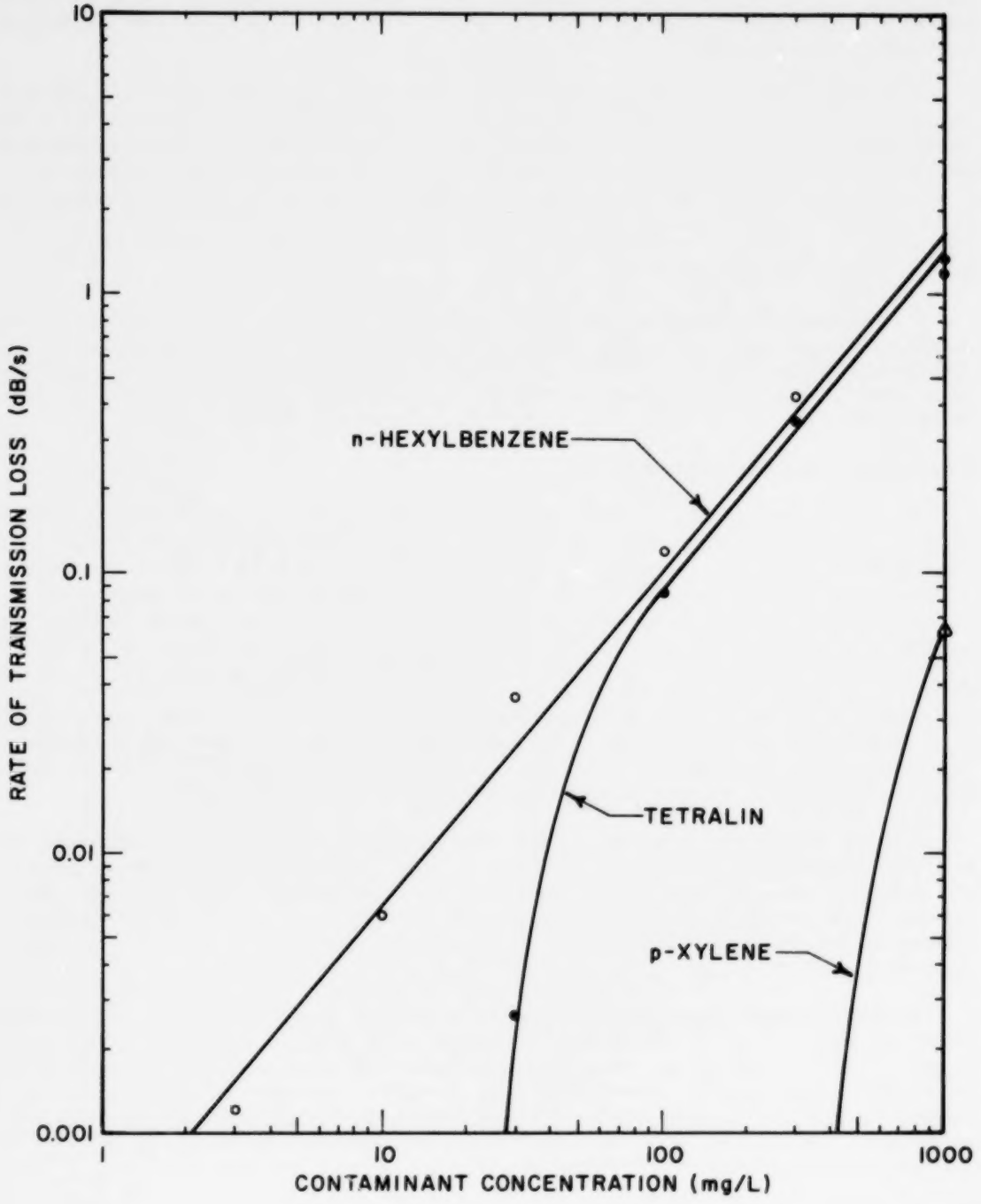

Figure 8. Response of Coiled Capillary-Tube Sensor Cell to Contaminants of Varying Solubility in Water

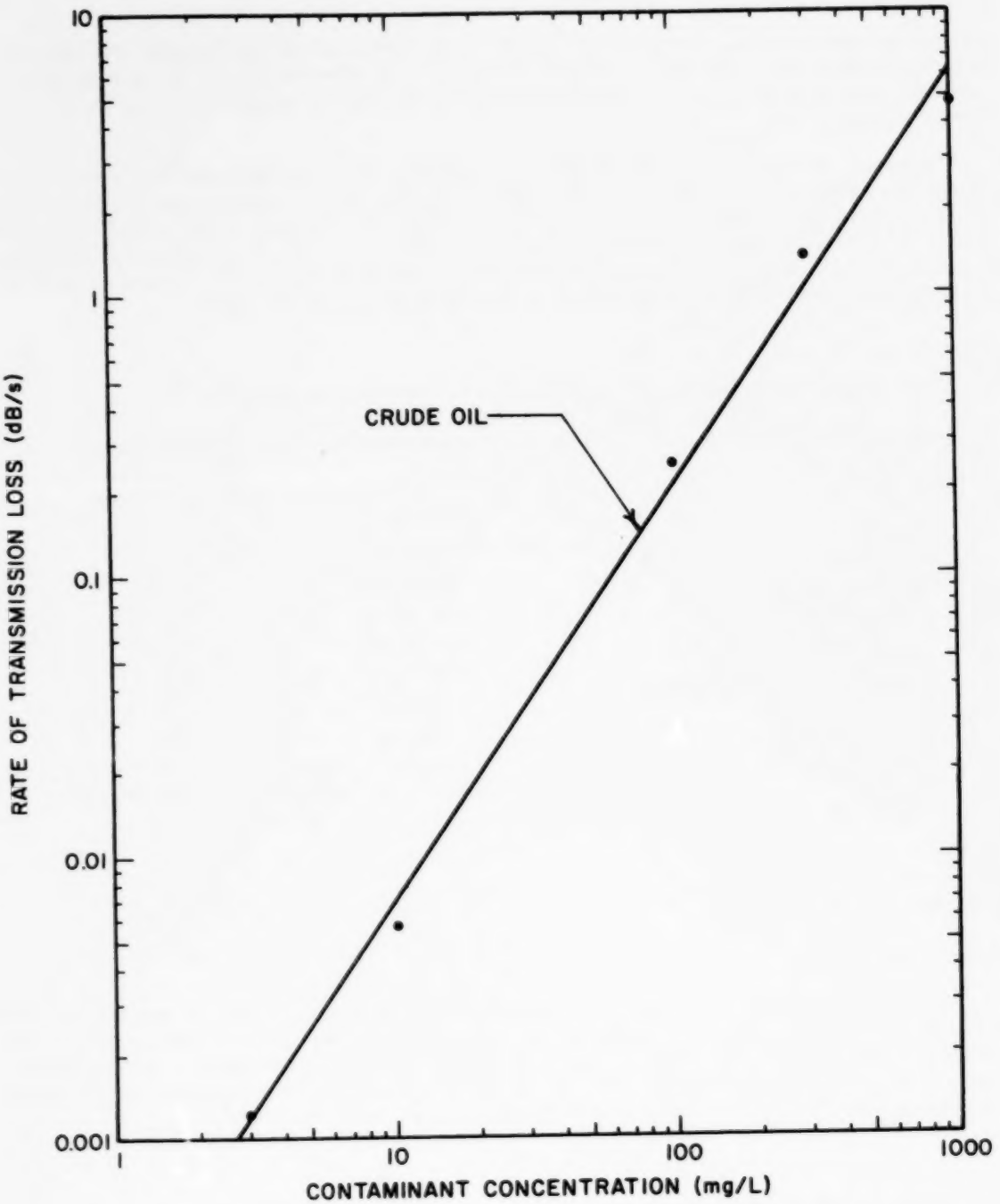

Figure 9. Response of Coiled Capillary-Tube Sensor Cell to Crude Oil in Water

p-xylene	200 mg/L
ethylbenzene	210mg/L

For each of these compounds, the detection threshold (as defined above) was slightly greater than the solubility figure as illustrated by the curve for p-xylene in Figure 8. Although still speculative, it may be possible to utilize this effect to actually measure solubility of various hydrocarbon compounds in water in the low part-per-million range.

Sensitivity (as defined in Appendix A) of the coiled capillary-tube sensor cell containing an organophilic optical fiber treated with octadecyltrichlorosilane was not the same for all contaminants tested. This is illustrated in Table III for contaminants which had detection thresholds of 100 mg/L or less. Sensitivity ranged from 0.15×10^{-3} for 2,6-dimethylstyrene and 1-phenylnaphthalene to 2.2×10^{-3} for 1-methylnaphthalene. Because sensitivity is not the same for all contaminants, it is necessary to calibrate the instrument in which the sensor cell is used for the particular contaminant or combination of contaminants expected.

TABLE III. SENSITIVITIES AND DETECTION THRESHOLDS OBSERVED FOR VARIOUS AROMATIC HYDROCARBON CONTAMINANTS

Contaminant	Sensitivity*	Approximate Detection Threshold (mg/L)
n-Hexylbenzene	1.97×10^{-3}	2
Cyclohexylbenzene	0.95×10^{-3}	<10
Heptadecylbenzene	0.34×10^{-3}	<10
3,3'-Dimethylbiphenyl	0.18×10^{-3}	<10
1-Phenylnaphthalene	0.15×10^{-3}	<10
1,2,3,4-Tetrahydronaphthalene(Tetralin)	1.58×10^{-3}	30
1-Methylnaphthalene	2.12×10^{-3}	40
2,6-Dimethylstyrene	0.15×10^{-3}	40
tert-Butylbenzene	0.17×10^{-3}	40

*Calculated using the formula derived in Appendix A.

PROTOTYPE INSTRUMENT

Sensor Cell

The sensor cell used in the previously described test apparatus was modified to provide a different mounting configuration and was incorporated in the prototype instrument. This cell employed a 0.13-mm (0.005-in.)-diameter fused-silica optical fiber approximately 1 m (39 in.) long. The fiber was treated with octadecyltrichlorosilane while installed in a coiled stainless steel capillary tube in accordance with the previously described process. Further details of the sensor cell are presented in a previous section.

Optics

Illumination for the optical fiber in the sensor cell is provided by a 2-mW helium-neon laser operating at the 632.8-nm (visible red) wavelength. The collimated beam from the laser is focused to a small spot by a 10X, 0.33-numerical aperture (N.A.) microscope objective. The objective lens is mounted in a 3-axis positioner to facilitate focusing and centering the small spot of light on the input end of the optical fiber.

Light emitted from the output end of the optical fiber falls on the sensitive area of a PIN (positive-intrinsic-negative) silicon photodiode. Ends of the optical fiber were cleaved using a sharp diamond scribe to initiate the break; this process produces smooth, flat surfaces at the ends of the fiber.

Signal Processing

It was determined experimentally that the logarithm of contaminant concentration is a linear function of the logarithm of the time rate of change of the logarithm of the light intensity emitted at the output end of the optical fiber. Accordingly, the signal processing system shown in block diagram form in Figure 10 was devised.

Photodiode output current, which is linearly proportional to intensity of light emitted from the output end of the optical fiber, passes into a logarithmic amplifier which delivers an output voltage proportional to the logarithm of the input current. The logarithmic signal is scaled and biased in a linear amplifier. Output voltage from this amplifier is impressed upon an analog differentiator which delivers an output voltage proportional to the time rate of change of its input voltage. Time constant (i.e., gain factor) of the differentiator is set by means of a range switch which facilitates selection of one of four full-scale sensitivity ranges. Differentiator output drives an analog meter mounted on the front panel of the prototype instrument. The meter is calibrated in units of decibels per second (dB/s) over the range from 0 to 1.0 dB/s, and the range switch provides multipliers of 0.01, 0.1, 1, and 10. System noise establishes a lower limit of 0.001 dB/s on the operating range of the system. In operation, two known concentrations of the contaminant to be analyzed are passed through the prototype instrument and scale readings are noted. Using a procedure described in the instruction manual for the prototype instrument, other concentrations of the same contaminant can be derived from subsequent meter readings.

Fluid Flow

A flow diagram of the prototype instrument is illustrated in Figure 11. The central component of the fluid handling system is the Reservoir which is used for temporary storage of the sample and regeneration solvents. Materials may be introduced into the reservoir through (1) a dip tube which fills the reservoir smoothly from the bottom or (2) a spray nozzle which directs the incoming material against the walls of the reservoir to improve cleaning action. Entry path into the reservoir is determined by the Reservoir Entry Selector, and the material entering the reservoir (*i.e.*, Sample, Solvent No. 1, Solvent No. 2, or Deionized Water) is determined by the Source Selector. Containers are provided for each of the four materials which can be admitted to the reservoir.

A compressed-air-operated Aspirator creates a partial vacuum in the reservoir, thus providing motive force for transferring fluids from their respective containers to the reservoir. The Air Control provides for directing compressed air into the aspirator during filling of the reservoir and into the reservoir for the purpose of forcing fluids through the Sensor Cell. An Air Supply Inlet fitting and an Air Supply Cutoff are provided for convenience in handling the compressed air supply, and gauges are provided for monitoring Air Supply Pressure and Reservoir Pressure.

Fluid flow out of the reservoir can be cutoff, directed into the sensor cell, or directed into the Water-Based Waste Receptacle by the Flow Control. Direction of flow through the sensor cell is determined by the Flow Direction Control which incorporates two mechanically ganged valves. During analysis and flushing the sensor cell with deionized water, flow through the sensor cell is in the forward direction, and waste fluid flows into the water-based waste receptacle. During regeneration, when either Solvent No. 1 or Solvent No. 2 is passing through the system, flow in the sensor cell is in the reverse direction, and waste fluids are delivered to the Hydrocarbon-Based Waste Receptacle. A Filter in the forward-flow inlet side of the sensor cell retains particulate matter which could clog the cell. During regeneration this filter is back-flushed along with the sensor cell.

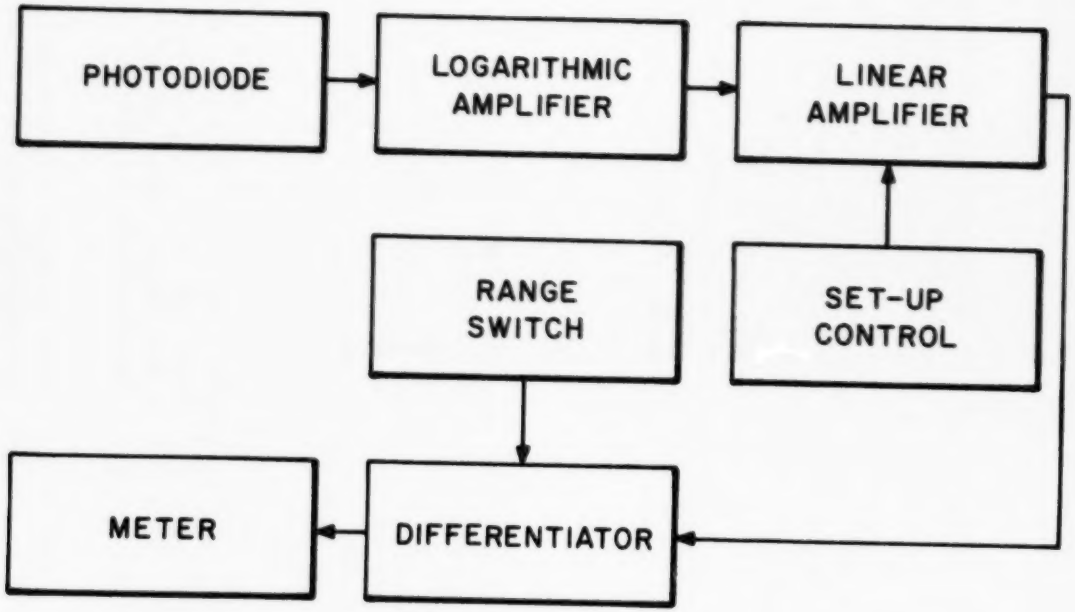

Figure 10. Block Diagram of Signal Processing System

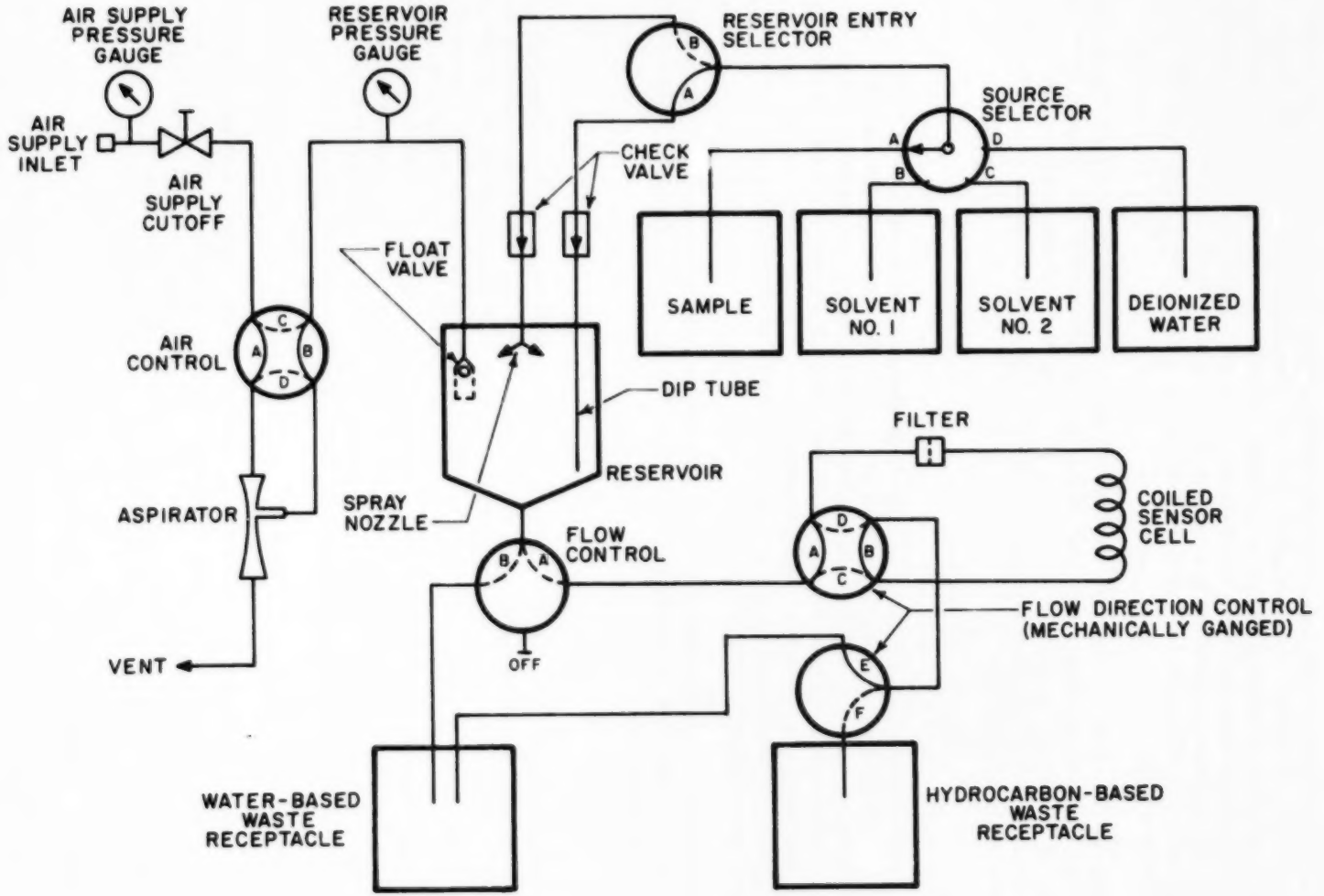

Figure 11. Flow Diagram of Prototype Instrument

Package

The prototype instrument is packaged in a metal cabinet which is 64 cm wide, 38 cm high, and 81 cm deep (25 × 15 × 32 in., respectively) as illustrated in Figure 12. Valves for controlling the flow of samples and cleaning solvents, electrical controls, and the output meter are mounted on the front panel of the cabinet. Containers for the cleaning solvents rest on a shelf attached to the rear panel of the cabinet. Services required for operation of the system include compressed air and electrical power, connectors for which are provided on the rear panel of the instrument. The sensor cell, laser, optical components and electrical components are housed within the cabinet.

Because the beam of light emitted by the laser is completely enclosed within the cabinet, the prototype instrument qualifies as a Class I laser system (Ref. 4) provided that the cabinet is not opened. A Class I laser system may contain a laser of a higher classification, but is considered exempt from operational controls provided that the laser is completely enclosed and laser light is not accessible to the skin or eyes of a human during normal equipment operation.

Operation

Procedures for operating the prototype instrument, designated Hydrocarbon-in-Water Monitor, Mk. I, are given in a separate instruction manual provided with the instrument. Briefly, the signal processing circuit is placed in the set-up mode, and preliminary electronic adjustment is made. Using the sequence of valve manipulations specified in the instruction manual, the reservoir is filled with the sample material, and the sample is caused to flow through the sensor cell. The signal processing circuit is placed in the run mode, and a meter reading is obtained. A calibration procedure, specified in the instruction manual, facilitates conversion of the meter reading to contaminant concentration.

After a stable meter reading has been obtained, the remaining sample is dumped to a waste receptacle, and regeneration is performed by passing two solvent systems sequentially through the sensor cell and, finally, flushing with deionized water.

Test Data

Tests of the prototype instrument were performed using n-hexylbenzene to which the experimental test apparatus responded well. A performance curve showing contaminant concentration as a function of meter reading in dB/s is presented in Figure 13. Threshold of detection for this material is between 3 and 10 mg/L which is not quite as good as obtained with the laboratory apparatus described earlier. The increased detection threshold was caused by system noise generated by (1) intensity fluctuations in the laser output and (2) variations in optical fiber transmission resulting from irregularities in flow through the sensor cell; such noise, even though of relatively low magnitude, is greatly accentuated by the differentiator in the signal processing circuit and makes accurate reading of the meter very difficult. Even so, a detection threshold of less than 10 mg/L is quite good for a first-generation portable instrument employing a new technology.

Organic Polymer Fibers

Several types of organic polymer fibers, including conventional polyethylene, linear (high-density) polyethylene, polypropylene and nylon, were obtained and tested to determine their potential as optical transmission devices and as oleophilic surfaces. None of these fibers exhibited adequate optical properties for use in an oil-in-water monitor device. Fibers of the same generic material from different manufacturers had similar properties. At present, an organic polymer fiber is not a satisfactory alternate to fused silica.

Fluoride Glass Investigation

For a hydrocarbon contaminant to be detectable by the organophilic optical fiber sensor, its index of refraction must be greater than the refractive index of the fiber material. Fused silica, with a refractive index

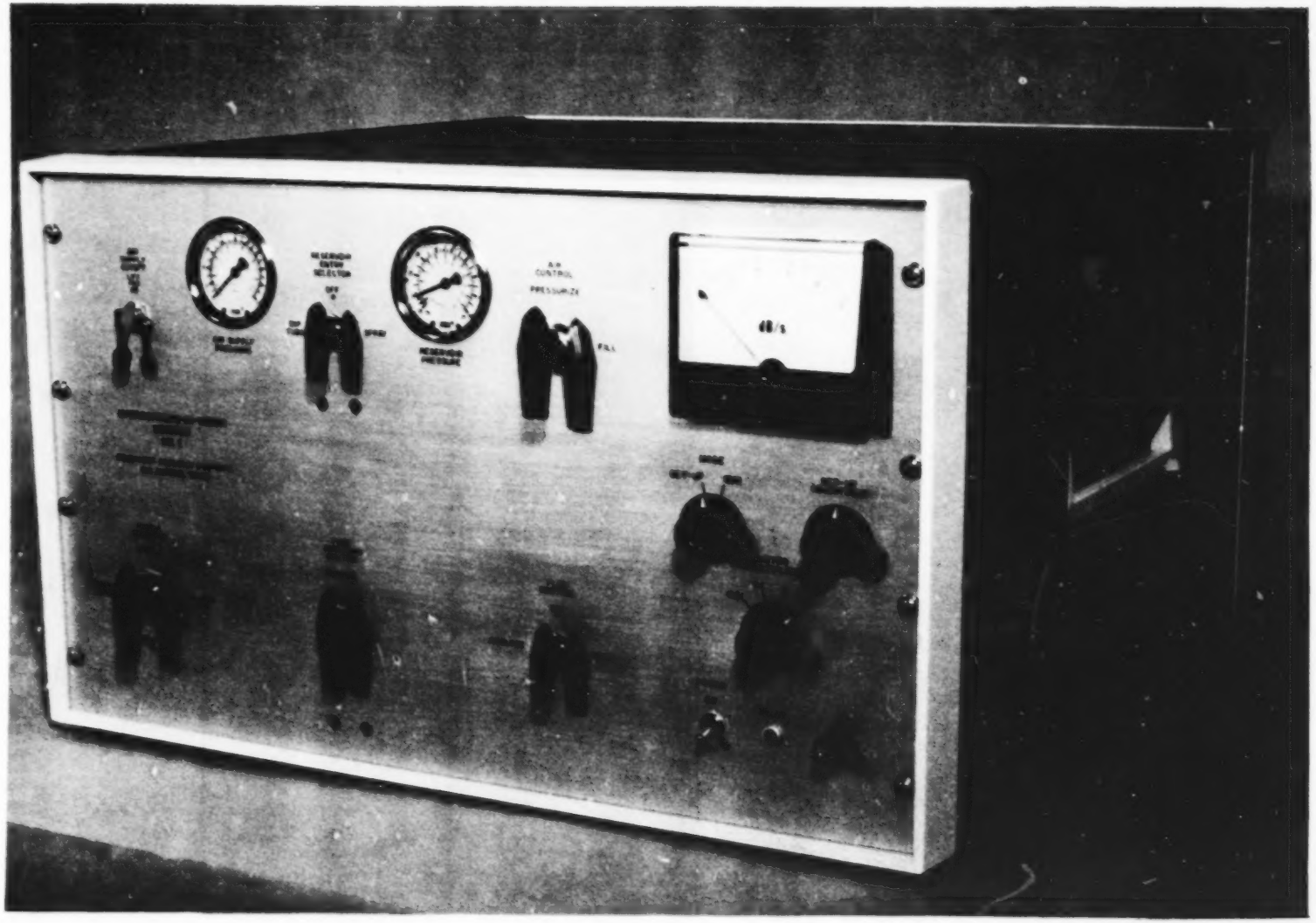

Figure 12. Hydrocarbon-in-Water Monitor, MK. I

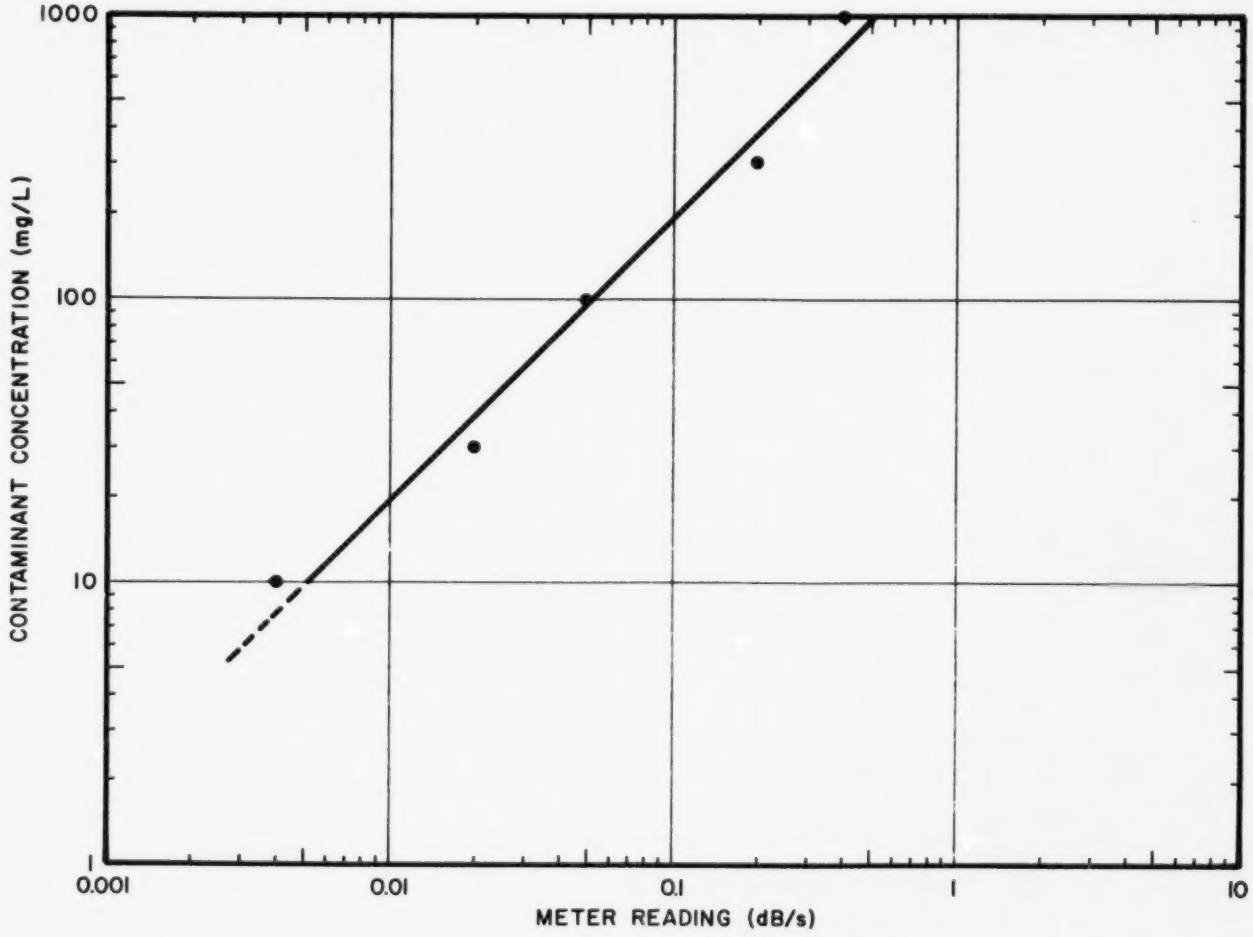

Figure 13. Response of Prototype Hydrocarbon-in-Water Monitor Instrument to n-Hexylbenzene

of 1.4585, has the lowest value of any commonly available material from which optical fibers can be made. This relatively high refractive index excludes from detection all paraffinic hydrocarbons, but most aromatic hydrocarbons are detectable by a fused-silica fiber.

Patents awarded in 1949 and 1950 (Refs. 5-8) describe a class of optical materials, referred to as "fluoride glasses", which were composed of fused fluorides of beryllium, aluminum, barium, magnesium and other metals in varying ratios. Indexes of refraction of fluoride glasses range from 1.3718 to 1.5140. If a fluoride glass having refractive index of 1.3718 could be satisfactorily formed into a durable optical fiber and organophilically treated, paraffinic hydrocarbons down to n-hexane could be detected.

Because of the potentially useful characteristics of fluoride glasses, attempts were made to obtain additional information. Contact was established with Eastman Kodak Company to which the referenced patents were assigned. The original inventor is no longer with the company, and because the patents have expired, Eastman Kodak has no interest in pursuing development of fluoride glass. Contact was also established with Corning Glass Works which has a current Department of Energy contract to develop and manufacture fluoride and fluorophosphate glasses for laser-fusion experiments at Lawrence Livermore Laboratories. This contract had been in existence for approximately 24 months, during which time Corning has established a plant and has begun experimentation with these materials. However, work is still in the research phase, and production has not been initiated; in fact, it will be at least one year before Corning is interested in other applications for fluoride glass.

Contact was also established with Galileo Electro-Optics Corp. which has personnel with limited experience in fluoride and fluorophosphate glasses. This company has a model shop for producing small quantities of special optical fibers, and interest was expressed in manufacturing sample fluoride and fluorophosphate glass optical fibers.

The principal constituent of fluoride glass is beryllium fluoride which is highly soluble in water. When this material is fused with fluorides of other metals in appropriate ratios, solubility of the resulting glass in bulk form is low. However, in the form of a small-diameter optical fiber immersed in flowing water, it is probable that fluoride glass would dissolve rapidly. In general, the fluorophosphate glasses, which have refractive indexes near 1.43, are significantly less soluble than fluoride glasses, and the higher-index fluoride glasses are less soluble than the low-index types.

The presently used organophilic treatment reagents react with oxygen atoms at the surface of the glass and probably are not suitable for treating a fluoride glass which has no oxygen-containing compounds in its composition. Thus, a completely new treatment system, which could accommodate fluoride glass chemistry, is necessary. From the preceeding, use of fluoride glass in an organophilic optical fiber oil-in-water monitor system is judged to be impractical at this time.

Evaluation of Light Sources

In the test apparatus used during Phases I and II of this program, a low-power helium-neon laser emitting red light at a wavelength of 632.8 nm was employed. A laser source was selected because it simplified coupling light into the input end of the optical fiber. However, there is no theoretical restriction on the type of light source. Accordingly, during this program, comparison was made of the relative intensity of light emitted from the output end of an optical fiber when the input end was illuminated by four different light sources. The fiber used in these tests was similar to that used in the sensor cell, that is, fiber diameter was 0.13 mm (0.005 in.), fiber length was 1.0 m (39.4 in.), and fiber material was fused silica. The sources evaluated included (1) a Hewlett Packard Type 5082-4658 red-light-emitting diode, (2) a Monsanto Type ME 7124 infrared-emitting diode, (3) a General Electric Type 1631X high-intensity incandescent lamp, and (4) a Spectra Physics Model 120 helium-neon laser. Important characteristics of each source are presented in Table IV.

Each source was tested in a number of different ways including (1) the input end of the fiber placed in contact with the exterior surface of the light source in the region of most intense emission, (2) the input end

TABLE IV. LIGHT SOURCE DATA

	Unit	Light-Emitting Diode	Infrared-Emitting Diode	Incandescent Lamp	Laser
Manufacturer	—	Hewlett Packard	Monsanto	General Electric	Spectra Physics
Type Number	—	5082-4658	ME 7124	1631X	120
Output Power	mW	0.31	2.2	—	5.0
Luminous Intensity	lm	—	—	290	—
Power Input	W	0.066	0.19	18	50
Power Efficiency	%	0.47	1.2	—	0.01
Luminous Efficiency	lm/W	—	—	16	—
Half-Power Beam Angle	°	35	12	180	0.057

of the fiber at the focal point of a 30-mm focal-length, f/1.6 plano-convex lens focused to produce minimum spot size, (3) the input end of the fiber at the focal point of a 12-mm focal-length f/0.67 aspheric condensing lens with focus adjusted for minimum spot size, and (4) the input end of the fiber at the focal point of a lens system comprising both of the previously described lenses with the aspheric lens nearest the source. It was found that light intensity emitted from the output end of the fiber was greatest by a factor of 100 when the laser source was used with any of the lenses.

Because light emission from a laser is highly coherent, it appears to originate from an almost dimensionless point source. As a result, energy from the laser can be focused to a very small point approximating the diffraction limit. All of the other sources were relatively extended and, therefore, energy from these sources could not be focused to a very small spot. Since the input aperture of the optical fiber was only 0.13 mm (0.005 in.) in diameter, capability of focusing a high percentage of the energy available from the source into a spot sufficiently small to enter the optical fiber aperture is extremely important. Even though some of the non-laser sources tested emitted sufficient energy to be useful, under the best conditions this energy could be focused to a spot no smaller than 1 mm (0.04 in.) in diameter; as a result, less than 2% of the available energy actually passed through the entrance aperture of the optical fiber so that the source was very inefficiently utilized. Accordingly, an inexpensive low-power helium-neon laser was selected as the light source to be included in the prototype instrument.

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APPENDIX A

DISCUSSION OF SENSITIVITY

When the response function of a system plots as a straight line on linear Cartesian coordinates, sensitivity of that system is defined as the slope of the straight line or, in other words, the derivative of the dependent variable (output) with respect to the independent variable (input). Since such a linear function has constant slope, sensitivity is a well defined, constant number. However, in the organophilic optical fiber oil-in-water monitor system discussed in this report, output (i.e., time rate of optical transmission change) as a function of input (i.e., contaminant concentration) plots as a straight line on logarithmic coordinates. Such a function, when plotted on linear Cartesian coordinates, is nonlinear and, therefore, does not have constant slope; thus, sensitivity is not constant and must be specified at a particular value of input. In this report, sensitivity figures are specified for a contaminant concentration of 1000 mg/L. The remainder of this Appendix derives the formula used for calculating sensitivity when the system response function plots as a straight line on logarithmic (*i.e.*, log-log) coordinates.

A function of the form

$$y = a^b x^m \tag{1}$$

plots as a straight line on logarithmic coordinates. By taking the logarithm (to the base a) of both sides of Equation (1), this functional form can also be expressed as

$$\log_a y = m \log_a x + b \tag{2}$$

This is the equation of a straight line. The slope m can be determined from the coordinates (x_1, y_1) and (x_2, y_2) of two points which lie on the straight line, and the intercept b can be determined from the coordinates (x,y) of any point on the line according to the following equations:

$$m = \frac{\log_a\left(\frac{y_2}{y_1}\right)}{\log_a\left(\frac{x_2}{x_1}\right)} \tag{3}$$

$$b = \log_a\left(\frac{y}{x^m}\right) \tag{4}$$

Note that the slope m is independent of the logarithmic base a; thus, m can be determined using either natural (base e) or common (base 10) logarithms.

Sensitivity is usually defined as the slope or derivative of the system response function. As will be shown in subsequent steps of this derivation, this concept of sensitivity can be applied to a function of the form indicated by Equation (1) or Equation (2) provided that sensitivity is calculated for a specified value of the input variable. Therefore, define sensitivity S as the derivative y′ of Equation (1).

$$S = y' = ma^b x^{m-1} \tag{5}$$

The slope m is a constant which can be calculated from Equation (3) above and thus requires no further discussion. The second term can be evaluated [using Equation (4)] as

$$a^b = a \exp(\log_a yx^{-m}) = yx^{-m} \tag{6}$$

Substituting Equation (6) in Equation (5) yields

$$S = m(yx^{-m})x^{m-1} = \frac{my}{x} \tag{7}$$

This result indicates that a value of sensitivity S can be calculated for any point (x,y) on the system response curve. To achieve comparable sensitivity figures, the selected point should always have the same value of the independent variable x (in this case, contaminant concentration).

EXAMPLE: Calculate sensitivity of sensor cell for tetralin using data given in the curve of Figure 8 in the body of the report.

SOLUTION: Select two points at extremes of the linear range of the curve:

$$x_1 = 1000 \text{ mg/L}$$
$$y_1 = 1.32 \text{ dB/s}$$
$$x_2 = 100 \text{ mg/L}$$
$$x_2 = 0.084 \text{ dB/s}$$

Compute slope from Equation (3)

$$m = \frac{\log\left(\frac{y_2}{y_1}\right)}{\log\left(\frac{x_2}{x_1}\right)} = \frac{\log\left(\frac{1.32}{0.084}\right)}{\log\left(\frac{1000}{100}\right)} = \frac{\log(15.7)}{\log(10)} = 1.196$$

Then compute sensitivity from Equation (7) using the values of x_1 and y_1 for x and y.

$$s = \frac{my}{x} = \frac{1.196 \times 1.32}{1000} = 1.53 \times 10^{-3}$$

APPENDIX B

DESCRIPTION OF CRUDE OIL USED IN TESTS

The crude oil used in evaluating the organophilic optical fiber sensor cell described in this report was taken from Sample AL6846-C. This sample is a black, opaque, viscous crude oil from Pearsall, Texas. The sample was separated into saturates, aromatics, and polars using a gravimetric liquid chromatographic procedure for oils. Olefins could not be obtained by this method. Saturates comprised 42% of the sample by weight, aromatics 25%, polars 18%, and 15% were lost. Other tests on the crude oil sample indicated a sulfur content of 1.7% by weight and a water content, determined by the Karl Fischer method, of 0.11% by weight. Specific gravity of the sample was 26.0° API at 15.6°C(60°F), and gross heat of combustion was 43.4 MJ/kg. Ash content was 0.02% by weight. Pour point was determined to be -10°C(14°F), and viscosity at 24°C (75°F) was 97 mm^2/s (97 centistokes).